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Memorandum

To: Trevor Baggiore

From: Colin Campbell

Date: January 20, 2005

Re: Supplemental Review of Yuma Refinery Soils and Vegetation Impacts

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As you know, pursuant to A.A.C. R18-2-407(I)(1), an analysis of the potential impacts of air pollutant emissions on soils and vegetation must be conducted before a Prevention of Significant Deterioration (PSD) permit can be issued for a new major stationary source. This requirement is applicable to the Arizona Clean Fuels Yuma ("ACF") refinery permit with respect to the following pollutants:

- Particulate matter (including PM_{10} and $PM_{2.5}$),
- Sulfur dioxide (SO_2),
- Nitrogen oxides (NO_X),
- Carbon monoxide (CO),
- Volatile organic compounds (VOC),
- Hydrogen sulfide (H_2S),
- Total reduced sulfur, and
- Reduced sulfur compounds.

The Technical Support Document (August 30, 2004) described the soils and vegetation impact analysis that was conducted prior to issuance of the proposed permit. This analysis included a consultation with the Arizona Department of Game and Fish and the U.S. Fish and Wildlife Service, through which no particularly sensitive soil or vegetation resources in the project vicinity were identified. As is customary in these circumstances, the Department and we relied heavily on the screening criteria in the U.S. EPA report *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals*.[1] This document establishes air pollutant concentrations that are generally viewed by U.S. EPA to be protective of soils and vegetation having significant commercial or recreational value, including agricultural crops, based on a broad review of pertinent scientific literature. The Department and we also relied on the secondary National Ambient Air Quality Standards (NAAQS),[2] which are established by U.S. EPA at levels that are protective of the public welfare, including agriculture.

During the public comment period for the Arizona Clean Fuels Yuma ("ACF") permit (Class I Permit No. 1001205), several commenters expressed concern with regard to the impact that the refinery's air

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[1] Smith, A.E., and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078)*. U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980.

[2] See, 40 CFR part 50.

pollutant emissions might have on agricultural crops grown near the refinery site. These commenters specifically identified lettuce as a crop of concern, and specifically identified aluminum, ammonia, cadmium, formaldehyde, lead, mercury, phenol, selenium, and silver as pollutants of concern. The commenters expressed concern with both phytotoxicity and human health effects. [3] None of these commenters identified any specific, scientific bases for their opinions regarding the inadequacy of the Department's analysis and, by extension, the *Screening Procedures* report. No information was provided that would tend to refute our preliminary conclusion that the refinery's emissions and the environmental impacts of those emissions are acceptable.

Nonetheless, in light of the significant value of agriculture in the Yuma County economy, and the significant number of comments on this issue, we have supplemented the soils and vegetation impacts review performed previously. The objective of this review was to determine whether there exists, in the scientific literature, any basis for concluding that the refinery's air pollutant emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. This memo will document the results of that supplemental review.

I. Scope and Methodology

A. Crops

We focused on the following crops that we believe are grown commercially in Yuma County:

- Broccoli (*Brassica oleracea*),
- Cantaloupe (*Cucumis melo*),
- Cotton (*Gossypium barbadense*),
- Cowpea (*Vigna unguiculata*),
- Lemon (*Citrus limon*),
- Lettuce (*Lactuca sativa*),
- Spinach (*Spinacia oleracea*), and
- Wheat (*Triticum aestivum*).

As discussed in detail below, there is a wealth of scientific data characterizing the effects of air pollutant emissions on some crops, notably lettuce and wheat, whereas there is a paucity of data for others.

B. Direct Phytotoxic Effects of Air Pollutants

Several gaseous air pollutants that will be emitted by the refinery are known to be phytotoxic to some plants at moderate to high concentrations in the ambient air. Of those gaseous pollutants subject to the PSD soils and vegetation impact analysis requirement at A.A.C. R18-2-407(I)(1), the pollutants of primary concern are SO_2, NO_X, and H_2S. These pollutants are included in our supplemental review.

[3] "Phytotoxicity" is toxicity to plants.

Carbon monoxide and volatile organic compounds (with the exception of ethylene) are generally not phytotoxic. [4, 5, 6, 7] Thus, these pollutants were generally not included in our supplemental review. We also did not include ozone in our supplemental review, although it is known to be the most important pollutant in terms of agricultural crop damage, because ozone is a regional pollutant and the refinery will not contribute appreciably to local ozone formation.

Finally, although they are not subject to the PSD soils and vegetation impact analysis requirement at A.A.C. R18-2-407(I)(1), we also included ammonia (NH_3) and tetrachloroethylene (C_2Cl_4) in our review, because those pollutants will be emitted by the refinery in relatively large quantities when compared to other non-PSD-regulated pollutants.

C. Indirect Effects of Air Pollutants due to Deposition to Soils

The refinery will emit small quantities of metals, and these metals will be deposited to some extent on land near the refinery. Much of this land is presently used for agricultural crop production. Several of the metals are Hazardous Air Pollutants (HAP), several are known to cause adverse human health effects, and several are known to be phytotoxic. Notwithstanding the fact that these air pollutants are not subject to the PSD soils and vegetation impact analysis requirement at A.A.C. R18-2-407(I)(1), our supplemental review included an analysis of the phytotoxic and human health effects that may occur as a result of deposition of metals to soils used for agricultural crop production, in order to address concerns with these potential effects.

As discussed in detail in Section II herein, there is a significant body of scholarly research into the phytotoxic effects that metals contained in soils may have on plants, including agricultural crops. There is also a significant body of research into the human health effects that may occur due to consumption of plants grown on soils containing metals. A number of regulations and guidelines have been established for the purpose of limiting the concentrations of metals in soils, including soils used for agricultural crop production. The primary stimulus for this research and for these regulations and guidelines is land application of sewage sludge, rather than air pollution, which contributes relatively little to soil contamination.

The regulations and guidelines established by foreign and domestic government agencies are intended to protect against adverse human health effects and adverse ecological effects (including phytotoxicity). Two general approaches have been used to establish deposition rate limits and soil concentration limits: preventing any accumulation of pollutants in waste-receiving soils, and maximizing the capacity of waste-receiving soils to assimilate, attenuate, and detoxify pollutants. The

[4] Smith, A.E., and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 11.

[5] *Air Quality Criteria for Carbon Monoxide.* U.S. Department of Health, Education, and Welfare, Public Health Service, National Air Pollution Control Administration. Washington, DC. March 1970. pp. 7-1 through 7-3.

[6] *Air Quality Criteria for Hydrocarbons.* U.S. Department of Health, Education, and Welfare, Public Health Service, National Air Pollution Control Administration. Washington, DC. March 1970. pp. 6-1 through 6-9.

[7] E.M. Hulzebos et al. "Phytotoxicity Studies with Lactuca Sativa in Soil and Nutrient Solutions." *Environmental Toxicology and Chemistry.* Volume 12. 1993. pp. 1079-1094.

first approach is based on the premise that soil can be used without any undue restriction if it is maintained free of contamination; if pollutants are artificially introduced (such as by land application of sewage sludge) and are allowed to accumulate in the soil, then, over the long term, the potential uses of the soil may become limited. This approach has been used by individual European countries. The second approach is based on the premise that the capacity of soils to detoxify pollutants should be utilized fully. This approach has been applied by the U.S. EPA and, recently, by the World Health Organization. [8] In Section II herein, the impacts from the refinery are documented and are shown to be less than the guideline levels established using both of these methods.

As the first step in evaluating the effects of metals deposition to soils near the refinery, we performed modeling and determined that the maximum dry PM deposition rate is 0.55 kilograms per hectare per year (kg/ha·yr). We have conservatively assumed that the wet deposition rate is equal to the dry deposition rate, for a total PM deposition rate of 1.1 kg/ha·yr. For each metal included in the supplemental review, we calculated the maximum predicted deposition rate as the product of the PM deposition rate and the ratio of modeled ambient concentrations for PM and the specific metal (as documented in Section VII of the Technical Support Document). For example, the cadmium deposition rate is calculated as follows:

$$DR_{Cd} = 1.1\ \text{kg/ha} \cdot \text{yr} \times \frac{0.000103\ \mu\text{g}/\text{m}^3}{1.33\ \mu\text{g}/\text{m}^3} = 0.000085\ \text{kg/ha} \cdot \text{yr}$$

where:

DR_{Cd}	= cadmium deposition rate
1.1 kg/ha·yr	= PM deposition rate
0.000103 μg/m^3	= modeled cadmium impact
1.33 μg/m^3	= modeled PM impact

We then calculated the deposition that would occur over a 100 year period at the deposition rate described above. For example, the 100-year cadmium deposition is calculated as follows:

$$D_{Cd} = 0.000085\ \text{kg/ha} \cdot \text{yr} \times 100\ \text{yrs} = 0.0085\ \text{kg/ha}$$

where:

D_{Cd}	= 100-year cadmium deposition
0.000085 kg/ha·yr	= cadmium deposition rate
100 years	= assumed pollutant accumulation period

Finally, we calculated the maximum predicted increases in soil concentration due to emissions from the refinery. For each metal, this value is calculated assuming that accumulation occurs over a 100 year period, using the 100-year deposition value described above, with no plant uptake or other pollutant removal, and using an assumed soil density of two million tons per hectare. For example, the soil cadmium concentration is calculated as follows:

[8] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. 19-41.

$$C_{Cd} = \frac{0.0085\ \text{kg/ha} \times 0.0011\ ^{\text{ton}}\!/_{\text{kg}}}{2{,}000{,}000\ ^{\text{tons}}\!/_{\text{ha}}} \times 10^{6} = 0.0000047\ \text{ppmw}$$

where:

C_{Cd}	= soil cadmium concentration, parts per million by weight
0.00085 kg/ha·yr	= cadmium deposition rate
0.0011 ton/kg	= conversion factor
2,000000 tons/ha	= assumed soil density

II. Results

A. Sulfur Dioxide

Based on the results of the air quality impacts analysis, as described in Table VII-6 of the Technical Support Document, the maximum predicted ambient SO_2 concentrations in the vicinity of the refinery are 115 μg/m^3 on a three-hour average; 52.3 μg/m^3 on a daily average; and 10.2 μg/m^3 on an annual average. These values are well below the secondary NAAQS of 1,300 μg/m^3 on a three-hour average and the minimum U.S. EPA screening values of 786 μg/m^3 on a three-hour average and 18 μg/m^3 on an annual average. [9] The agricultural crops for which the minimum U.S. EPA screening values are listed as being protective include broccoli, cantaloupe, cotton, lettuce, spinach, wheat, and citrus species (which include lemon). [10] The only crop identified in Section I.A herein that is not specifically listed in the *Screening Procedures* report is cowpea.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that (a) the secondary NAAQS and the minimum U.S. EPA screening values are not protective of any of the crops identified in Section I.A herein, or (b) the refinery's SO_2 emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. A summary of our findings follows.

In 2000, the World Health Organization, in conjunction with the United Nations Economic Commission for Europe, reaffirmed its SO_2 guideline concentration value of 30 μg/m^3. This value applies both on an annual average basis and, "in view of the increased sensitivity of crops growing slowly under winter conditions," on a winter-average basis (from October 1 through March 31). The 30 μg/m^3 value is based on protecting the most sensitive types of agricultural crops for which good quality data are available. Also in 2000, the World Health Organization abandoned the previous short-term SO_2 guideline concentration value of 100 μg/m^3 on a daily average, "in view of further evidence that peak concentrations are not significant compared with the accumulated dose." [11]

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[9] Smith, A.E., and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 11.

[10] Ibid. p. 61.

[11] *Air Quality Guidelines for Europe, 2nd Ed.* World Health Organization, Regional Office for Europe. Copenhagen, Denmark. 2000. pp. 219-229.

Studies performed in India in 1998 and 2002 both found that wheat plants exhibited yield decreases and other phytotoxic effects when continuously exposed to SO_2 at a concentration of 160 µg/m^3. [12, 13]

An Australian study published in 1990 found that wheat plants did not exhibit any phytotoxic effects when intermittently exposed to SO_2 at a concentration of 11 µg/m^3 for a period of 79 days, but did exhibit phytotoxic effects at an SO_2 concentration of 112 µg/m^3 for the same duration. [14]

An American study published in 1987 found that yield of wheat plants was unaffected by intermittent exposure to SO_2 at concentrations as high as 966 µg/m^3 for a period of 36 days. The same findings were made at four different average ozone concentration levels ranging from 0.027 ppmv to 0.096 ppmv. In this study, the SO_2 exposure period was initiated after flowering of the wheat plants. [15]

An Australian study published in 1988 found that yield of wheat plants was unaffected by continuous exposure to SO_2 at concentrations as high as 267 µg/m^3 for a period of 90 days. [16]

A 1988 study performed for the California Air Resources Board found that both lettuce and wheat plants exhibited phytotoxic effects when continuously exposed to SO_2 at a concentration of 319 µg/m^3 under ambient humidity. This study also found that lettuce plants experienced increased yield when exposed to the same SO_2 concentration and elevated humidity (approximately 40 percent above ambient relative humidity). [17]

A 1985 study performed for the California Air Resources Board found that lettuce plants exhibited no phytotoxic effects when continuously exposed to SO_2 at concentrations as high as 393 µg/m^3. The same study found that wheat plants were adversely affected by continuous exposure to SO_2 at concentrations as low as 79 µg/m^3. [18]

A German study, published in 1968, evaluated 18 important agricultural crops for phytotoxic effects of long-term SO_2 exposure at varying concentrations. This study found that wheat plants are highly sensitive to SO_2 exposure, with a threshold average concentration of approximately 27 µg/m^3 for phytotoxic effects. Spinach was found to be highly insensitive, with only five percent decrease in yield

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[12] Agrawal, M., and S.S. Deepak. "Physiological and Biochemical Responses of Two Cultivars of Wheat to Elevated Levels of CO_2 and SO_2, Singly and in Combination." *Environmental Pollution.* Volume 121. 2003. pp. 189-197.

[13] Agrawal, M., and S.S. Deepak. "Growth and Yield Responses of Wheat Plants to Elevated Levels of CO_2 and SO_2, Singly and in Combination." *Environmental Pollution.* Volume 104. 1999. pp. 411-419.

[14] S.A. Wilson and F. Murray. "SO_2-Induced Growth Reductions and Sulphur Accumulation in Wheat." *Environmental Pollution.* Volume 66. 1990. pp. 179-191.

[15] R.J. Kohut et al. "Effects of Ozone and Sulfur Dioxide on Yield of Winter Wheat." *Phytopathology.* Volume 77. 1987. pp. 71-74.

[16] F. Murray and S.A. Wilson. "The Joint Action of Sulphur Dioxide and Hydrogen Fluoride on the Yield and Quality of Wheat and Barley." *Environmental Pollution.* Volume 55. 1988. pp. 239-249.

[17] Thompson, C.R., and D.M. Olszyk. *Interaction of Humidity and Air Pollutants on Vegetation.* University of California. Riverside, CA. March 1988.

[18] Thompson, C.R. *Effects of SO_2 on Growth and Yield of Winter Crops Grown in California.* University of California. Riverside, CA. September 1985.

at a mean long-term concentration of 375 μg/m^3 and increased yield at a long-term average concentration of 27 μg/m^3. [19]

Another German study, published in 1967, found that spinach plants and three cultivars of lettuce plants all exhibited phytotoxic effects when continuously exposed to SO_2 at mean concentrations ranging from 380 to 470 μg/m^3. When continuously exposed to SO_2 at mean concentrations ranging from 330 to 340 μg/m^3, the spinach plants and one of the three cultivars of lettuce plants exhibited phytotoxic effects, but the other two cultivars of lettuce plants did not exhibit any statistically significant effects. [20]

Nothing in the scientific literature identified during this supplemental review would indicate that the secondary NAAQS and the minimum U.S. EPA screening values are not protective of any of the crops identified in Section I.A herein. The maximum predicted SO_2 concentration is well below the secondary NAAQS, the minimum U.S. EPA screening values, guideline concentration values established by foreign governmental agencies, and concentrations that are identified in the literature as being harmful to crops.

B. Nitrogen Oxides

NO_X includes both nitric oxide (NO) and nitrogen dioxide (NO_2), and much of the scientific literature treats these two pollutants separately.

Based on the results of the air quality impacts analysis, as described in Table VII-6 of the Technical Support Document, the maximum predicted impact on ambient NO_X concentration due to emissions from the refinery is 0.6 μg/m^3 on an annual average. Assuming a background concentration of 4 μg/m^3, the maximum predicted ambient NO_X concentration in the vicinity of the refinery is 5 μg/m^3 on an annual average. This value is well below the secondary NAAQS of 100 μg/m^3 on an annual average and the minimum U.S. EPA screening value of 94 μg/m^3 on an annual average. Both the secondary NAAQS and the screening value are expressed in terms of NO_2; there are no NAAQS or screening values for NO. [21] The agricultural crops for which the minimum U.S. EPA screening value is listed as being protective include broccoli, cotton, lettuce, wheat, and citrus species (which include lemon). [22] The crops identified in Section I.A herein that are not specifically listed in the *Screening Procedures* report are cantaloupe, cowpea, and spinach.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that (a) the secondary NAAQS and the minimum U.S. EPA screening value are not protective of any of the crops identified in Section I.A herein, or (b) the refinery's NO_X emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. A summary of our findings follows.

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[19] Godzik, S., and S.V. Krupa. "Effects of Sulphur Dioxide on the Growth and Yield of Agricultural and Horticultural Crops." In *Effects of Gaseous Air Pollution in Agriculture and Horticulture.* M.H. Unsworth and D.P. Ormrod, eds. 1982.
[20] Ibid.
[21] Smith, A.E., J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 11.
[22] Ibid. p. 61.

In 2000, the World Health Organization instituted a NO_X guideline concentration value of 30 μg/m^3 on an annual average (including both NO and NO_2, expressed as NO_2). They declined to institute a short-term value, saying "[t]here are insufficient data to provide these levels with confidence at present," but indicated that current evidence would suggest a guideline NO_X concentration value of about 75 μg/m^3 on a daily average. The guideline concentration value is intended to be protective of all classes of vegetation under all environmental conditions. [23]

A Swiss study published in 1995 found that wheat plants exhibited no phytotoxic effects due to long-term exposure to NO at a concentration of 86 μg/m^3 (132 μg/m^3 as NO_2) in the presence of ambient ozone levels (long-term mean approximately 0.04 ppmv), or due to long-term exposure to NO at a concentration of 50 μg/m^3 (77 μg/m^3 as NO_2) in the presence of elevated ozone levels (long-term mean approximately 0.06 ppmv). [24]

A British study published in 1994 found that lettuce plants exhibited significant but reversible phytotoxic effects when exposed to NO for short periods at a concentration of 2,500 μg/m^3 (3,800 μg/m^3 as NO_2) in the presence of elevated CO_2 levels (approximately 1,000 ppmv). [25]

A British study published in 1989 found that lettuce plants exhibited phytotoxic effects as a result of long-term exposure to NO at concentrations ranging from 600 to 2,500 μg/m^3 (1,000 to 3,800 μg/m^3 as NO_2) in the presence of elevated CO_2 levels (approximately 1,200 ppmv). [26]

A Japanese study published in 1988 found that spinach plants did not exhibit any phytotoxic effects when exposed to NO_2 at concentrations as high as 15,000 μg/m^3 for short periods; at this concentration, phytotoxic effects began to emerge only after 20 hours of exposure. [27]

An American study published in 1987 found that wheat plants exhibited slight phytotoxic effects when intermittently exposed to NO_X at a concentration of 150 μg/m^3 for a period of 38 days. [28]

An American study published in 1979 found that cotton plants did not exhibit any phytotoxic effects when exposed to NO_2 at a concentration of 31,000 μg/m^3 for a period of one hour, but did exhibit

[23] *Air Quality Guidelines for Europe, 2nd Ed.* World Health Organization, Regional Office for Europe. Copenhagen, Denmark. 2000. pp. 230-233.
[24] Nussbaum, S., et al. "Effects of Nitric Oxide and Ozone on Spring Wheat (*Triticum aestivum*). *Water, Air & Soil Pollution*. Volume 85. 1995. pp. 1449-1454.
[25] Caporn, S.J.M, et al. "Canopy Photosynthesis of CO_2-enriched Lettuce (*Lactuca sativa* L.). Response to Short-term Changes in CO_2, Temperature, and Oxides of Nitrogen." *New Phytologist*. Volume 126. 1994. pp. 45-52.
[26] Caporn, S.J.M. "The Effects of Oxides of Nitrogen and Carbon Dioxide Enrichment on Photosynthesis and Growth of Lettuce (*Lactuca sativa* L.)." *New Phytologist*. Volume 111. 1989. pp. 473-481.
[27] Shu-Wen Yu et al. "Response of Spinach and Kidney Bean Plants to Nitrogen Dioxide." *Environmental Pollution.* Volume 55. 1988. pp. 1-13.
[28] *Air Quality Criteria for Oxides of Nitrogen. Volume II of III. (EPA-600/8-91-049b).* U.S. EPA, Office of Research and Development, Environmental Criteria and Assessment Office. Research Triangle Park, NC. August 1993. p. 9B-10.

significant phytotoxic effects when exposed to NO_2 at a concentration of 61,000 μg/m^3 for the same duration. [29]

The same study found that broccoli plants did not exhibit any phytotoxic effects when exposed to NO_2 at a concentration of 19,000 μg/m^3 for a period of two hours, or to a concentration of 10,000 μg/m^3 for a period of seven hours, but did exhibit significant phytotoxic effects when exposed to NO_2 at a concentration of 29,000 μg/m^3 for a period of one hour. [30]

A German study published in 1975 found that wheat plants did not exhibit any phytotoxic effects when intermittently exposed to NO_X at concentrations as high as 1,900 μg/m^3 for a period of 40 days. [31]

An American study published in 1964 found that cotton plants did not exhibit any phytotoxic effects when continuously exposed to NO_2 at a concentration of 1,900 μg/m^3 for a period of 12 hours. The same study found that cotton plants exhibited slight phytotoxic effects when continuously exposed to NO_2 at a concentration of 1,900 μg/m^3 for a period of 48 hours or to a concentration of 6,600 μg/m^3 for a period of 21 hours. [32]

Nothing in the scientific literature identified during this supplemental review would indicate that the secondary NAAQS and the minimum annual U.S. EPA screening value are not protective of any of the crops identified in Section I.A herein. The maximum predicted NO_X concentration is well below the secondary NAAQS, the minimum U.S. EPA screening value, guideline concentration values established by foreign governmental agencies, and concentrations that are identified in the literature as being harmful to crops.

C. Hydrogen Sulfide

Based on the results of the air quality impacts analysis, as described in Table VII-7 of the Technical Support Document, the maximum predicted impacts on ambient H_2S concentration due to emissions from the refinery are 84.6 μg/m^3 on a one-hour average and 7.09 μg/m^3 on a daily average. These values are well below the minimum U.S. EPA screening value of 28,000 μg/m^3 on a four-hour average.[33] There are no NAAQS for H_2S.

[29] *Air Quality Criteria for Oxides of Nitrogen. (EPA-600/8-82-026).* U.S. EPA, Office of Research and Development, Environmental Criteria and Assessment Office. Research Triangle Park, NC. September 1982. p. 12-31.

[30] *Air Quality Criteria for Oxides of Nitrogen. (EPA-600/8-82-026).* U.S. EPA, Office of Research and Development, Environmental Criteria and Assessment Office. Research Triangle Park, NC. September 1982. p. 12-33.

[31] *Air Quality Criteria for Oxides of Nitrogen. Volume II of III. (EPA-600/8-91-049b).* U.S. EPA, Office of Research and Development, Environmental Criteria and Assessment Office. Research Triangle Park, NC. August 1993. p. 9B-9.

[32] *Air Quality Criteria for Oxides of Nitrogen. (EPA-600/8-82-026).* U.S. EPA, Office of Research and Development, Environmental Criteria and Assessment Office. Research Triangle Park, NC. September 1982. p. 12-30.

[33] Smith, A.E., J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 11.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's H_2S emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. We found only two references discussing the phytotoxicity of this pollutant, and one refers to the same study cited by the *Screening Procedures* report. This study, published in 1978, evaluated the effects on lettuce plants due to prolonged exposure to H_2S at various concentrations. The results of this study showed that yield increased when exposed to H_2S at concentrations of 42 $\mu g/m^3$ and 139 $\mu g/m^3$. Lettuce plants exhibited signs of phytotoxic effects when exposed to H_2S at a concentration of 417 $\mu g/m^3$. [34]

The second reference describes a Dutch study, published in 1997, evaluating the effects of H_2S exposure in kale plants (*Brassica oleracea*, but a different cultivar than broccoli) and barley plants (*Hordeum vulgare*). This study found that neither barley nor kale plants exhibited any signs of phytotoxicity due to continuous exposure to H_2S at a concentration of 350 $\mu g/m^3$ when grown in soil containing normal sulfate levels. The study also found that both barley plants and kale plants grew normally when continuously exposed to H_2S at a concentration of 350 $\mu g/m^3$ in sulfur-deficient soil, but grew poorly when grown in the same soil without H_2S exposure. [35]

Nothing in the scientific literature identified during this supplemental review would indicate that the minimum U.S. EPA screening value is not protective of any of the crops identified in Section I.A herein. The maximum predicted H_2S concentration is well below the minimum U.S. EPA screening value and concentrations that are identified in the literature as being harmful to crops.

D. Ammonia

Based on the results of the air quality impacts analysis, as described in Table VII-7 of the Technical Support Document, the maximum predicted impacts on ambient NH_3 concentration due to emissions from the refinery are 2.49 $\mu g/m^3$ on a one-hour average and 0.497 $\mu g/m^3$ on a daily average. [36] There are no NAAQS or U.S. EPA screening values for NH_3.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's NH_3 emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. A summary of our findings follows.

In 2000, the World Health Organization instituted a NH_3 guideline concentration value of 8 $\mu g/m^3$ on an annual average. They declined to institute a short-term value, saying "[t]here are insufficient data to provide these levels with confidence at present," but indicated that current evidence would suggest a

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[34] Cowling, D.W., and M.J. Koziol. "Mineral Nutrition and Plant Response to Air Pollutants." In *Effects of Gaseous Air Pollution in Agriculture and Horticulture.* M.H. Unsworth and D.P. Ormrod, eds. 1982.

[35] C.E.E. Stuiver and L.J. De Kok. "Atmospheric H_2S as Sulphur Source for Sulphur Deprived *Brassica Oleracea* L. and *Hordeum Vulgare* L." In *Sulphur Metabolism in Higher Plants*. W.J. Cram, et al., editors. 1997. pp. 293-294.

[36] Table VII-7 in the August 30, 2004 version of the Technical Support Document contains a typographical error. The table shows a modeled concentration of "2.49E+01" $\mu g/m^3$ on a one-hour average, which is equivalent to 24.9 $\mu g/m^3$; the correct value is 2.49 $\mu g/m^3$.

guideline NH_3 concentration value of about 270 μg/m^3 on a daily average. The guideline concentration value is intended to be protective of all classes of vegetation under all environmental conditions. [37]

A Dutch study published in 1995 found that wheat plants exhibited increased yield and no phytotoxic effects as a result of exposure to NH_3 at a concentration of 1,100 μg/m^3 for a period of 36 days, including 14 days at moderate temperature and 22 days at low temperature. [38]

A German study published in 1990 found that spinach plants exhibited phytotoxic effects as a result of exposure to NH_3 at a concentration of 2,000 μg/m^3 for a period of 14 days; at an NH_3 concentration of 5,000 μg/m^3, spinach plants were found to exhibit phytotoxic effects beginning after 2.5 days of exposure. [39]

A Dutch study published in 1982 evaluated the effects of ammonia exposure on several agricultural crops and found the following: [40]

- Cauliflower (*Brassica oleracea*, but a different cultivar than broccoli) exhibited phytotoxic effects as a result of exposure to NH_3 at a concentration of 600 μg/m^3 for a period of 16 days;
- Lettuce plants did not exhibit any phytotoxic effects as a result of exposure to NH_3 at concentrations of 2,000 μg/m^3 or 4,200 μg/m^3 for a period of two days, but did exhibit phytotoxic effects when exposed to NH_3 at the same concentrations for a period of six days.

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's NH_3 emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. The maximum predicted NH_3 concentration is well below guideline concentration values established by foreign governmental agencies and concentrations that are identified in the literature as being harmful to crops.

E. Tetrachloroethylene

Based on the results of the air quality impacts analysis, as described in Table VII-7 of the Technical Support Document, the maximum predicted impacts on ambient tetrachloroethylene concentration due to emissions from the refinery are 1.70 μg/m^3 on a one-hour average, 0.369 μg/m^3 on a daily average, and 0.0282 μg/m^3 on an annual average. There are no NAAQS or U.S. EPA screening values for tetrachloroethylene.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's tetrachloroethylene emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. We found only one technical paper, published in 2003, discussing the phytotoxicity of this pollutant. According to this paper, a 1991 German study found that spruce pine needles were adversely affected by short-term exposure at a concentration of

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[37] *Air Quality Guidelines for Europe, 2nd Ed.* World Health Organization, Regional Office for Europe. Copenhagen, Denmark. 2000. pp. 230-233.
[38] Clement, J.M.A.M., et al. "Short-term Exposure to Atmospheric Ammonia Does Not Affect Low-temperature Hardening of Winter Wheat." *New Phytologist*. Volume 131. 1995. pp. 345-351.
[39] A. Fangmeier. "Effects of Atmospheric Ammonia on Vegetation – A Review." *Environmental Pollution.* Volume 86. 1994. pp. 43-82.
[40] Ibid.

172 μg/m^3. The paper also discusses a Dutch study published in 2000 that evaluated the effects of long-term exposure to six concentrations of tetrachloroethylene in three agricultural crop species, three tree species, three wild herbaceous species, and three mosses. This study found that the most sensitive of these twelve species was the bean (*Phaseolus vulgaris*), for which phytotoxic effects were observed at concentrations of 46 μg/m^3 and higher. [41]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's tetrachloroethylene emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. The maximum predicted tetrachloroethylene concentration is well below the concentrations that are identified in the literature as being harmful to crops.

F. Aluminum

The maximum predicted deposition rate of aluminum is 0.81 kg/ha·yr, the maximum 100-year deposition is 81 kg/ha, and the maximum 100-year increase in soil concentration is 0.045 parts per million by weight (ppmw). There are no NAAQS or U.S. EPA screening values for aluminum.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of aluminum will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to aluminum uptake by agricultural crops. A summary of our findings follows.

Naturally occurring aluminum concentrations in soils are generally in the range 4,500 ppmw to 100,000 ppmw. [42]

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 50 ppmw for aluminum. [43] This value is primarily based on phytotoxicity of white clover [44] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

According to a 1966 textbook, a study published in 1953 found that lettuce plants exhibited phytotoxic effects when grown in soil suspension with an aluminum concentration of 0.7 ppmw. [45]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's aluminum emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site. The maximum predicted aluminum deposition rate will not lead to soil

[41] J.N. Cape. "Effects of Airborne Volatile Organic Compounds on Plants." *Environmental Pollution.* Volume 122. 2003. pp. 145-157.
[42] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.
[43] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[44] Ibid. p. 3-1.
[45] P.F. Pratt. "Aluminum." In Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences. Riverside, CA. 1966. p. 9.

concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

G. Cadmium

The maximum predicted deposition rate of cadmium is 0.000085 kg/ha·yr, the maximum 100-year deposition is 0.0085 kg/ha, and the maximum 100-year increase in soil concentration is 0.0000047 ppmw. The concentration value is more than five orders of magnitude below the minimum U.S. EPA screening value of 2.5 ppmw.[46] There are no NAAQS for cadmium.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of cadmium will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to aluminum uptake by agricultural crops. A summary of our findings follows.

In general, cadmium is the metal of primary concern as a contaminant in soils used for agricultural crop production due to its relative ease of uptake by plants and its high level of toxicity to humans.[47, 48, 49] Unlike other metals, cadmium can be accumulated in several food crops at levels that are potentially hazardous to human health without the plants first suffering severe phytotoxic effects.[50] Lettuce is used frequently in studies of cadmium uptake, phytotoxicity, and human health risk because it accumulates cadmium from contaminated soil more readily than most other agricultural crops.[51, 52, 53, 54]

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[46] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.
[47] M.P.C. de Vries and K.G. Tiller. "The Effect of Sludges from Two Adelaide Sewage Treatment Plants on the Growth of and Heavy Metal Concentrations in Lettuce." *Australian Journal of Experimental Agriculture and Animal Husbandry.* Volume 18. February 1978. pp. 143-147.
[48] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 62.
[49] S.J. Kim et al. "Relative Concentrations of Cadmium and Zinc in Tissue of Selected Food Plants Grown on Sludge-Treated Soils." *Journal of Environmental Quality.* Volume 17. 1988. pp. 568-573.
[50] *Use of Reclaimed Water and Sludge in Food Crop Production.* National Research Council, Water Science and Technology Board. Washington, DC. 1996. p. 109.
[51] P.M. Giordano et al. "Soil Temperature Effects on Uptake of Cadmium and Zinc by Vegetables Grown on Sludge-amended Soil." *Journal of Environmental Quality.* Volume 8. 1979. pp. 233-236.
[52] D.M.M. Adema and L. Henzen. "A Comparison of Plant Toxicities of Some Industrial Chemicals in Soil Culture and Soilless Culture." *Ecotoxicology and Environmental Safety.* Volume 18. 1989. pp. 219-229.
[53] S.J. Kim et al. "Relative Concentrations of Cadmium and Zinc in Tissue of Selected Food Plants Grown on Sludge-Treated Soils." *Journal of Environmental Quality.* Volume 17. 1988. pp. 568-573.
[54] F. Haghiri. "Cadmium Uptake by Plants." *Journal of Environmental Quality.* Volume 2. 1973. pp. 93-95.

Naturally occurring cadmium concentrations in soils are generally in the range 0.01 ppmw to 2.7 ppmw, with a typical concentration of 0.4 ppmw. [55]

In 2002, the World Health Organization adopted a maximum soil concentration screening value of 3.92 ppmw for cadmium. [56] In establishing this value, the organization identified guideline values established by thirteen different governments, including the U.S. and the European Union. The most stringent limit is a total deposition threshold of 0.4 kg/ha, established by the governments of Denmark and Sweden. [57] This limit is approximately 50 times the maximum deposition expected from the refinery over a 100-year period.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 4 ppmw for cadmium. [58] This value is based on phytotoxicity of several plants, including spinach, [59] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

In Canada, the maximum acceptable level for cumulative cadmium additions to soil is 4 kg/ha. [60] This standard, which was initially adopted in 1979 and was most recently reaffirmed in 1997, is intended to protect against risk to humans, plants, and animals. [61] The Canadian standard is approximately 500 times the maximum deposition expected from the refinery over a 100-year period.

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for cadmium of 39 kg/ha. This limit is based on the level that was found to be safe for a child ingesting biosolids, which is the most restrictive of all exposure pathways evaluated. For the "human home gardener" exposure pathway, assuming a lifetime of eating vegetables grown in cadmium-contaminated soil, U.S. EPA determined that the maximum cumulative loading limit would be 120 kg/ha. A loading limit based on phytotoxicity was not determined. [62]

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[55] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.
[56] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.
[57] Ibid. p. 31.
[58] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[59] Ibid. pp. 3-8 through 3-10.
[60] *Guidelines to the Fertilizers Act and Regulations, 2nd Ed.* Agriculture and Agri-Food Canada. Nepean, Ontario, Canada. November 1996. p. 3-3.
[61] Ibid.
[62] *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.

American studies published in 2003 and 2004 found that yield of lettuce plants was not affected by addition of cadmium to soil at rates as high as 1.4 kg/ha, which was the highest cadmium addition rate evaluated. [63, 64]

A Hungarian study presented in 2002 found that lettuce plants did not exhibit any phytotoxic effects when grown in soil with a cadmium concentration as high as 17 ppmw, which was the highest cadmium concentration evaluated. [65]

A Korean study presented in 2002 found that lettuce plants did not exhibit any phytotoxic effects when grown in soil with a cadmium concentration as high as 10 ppmw, but did exhibit significant phytotoxic effects at a cadmium concentration of 25 ppmw. [66]

A study commissioned by the Washington State Department of Agriculture and published in 2001 found that yield of lettuce plants was not affected by addition of cadmium to soil at rates as high as 3.6 kg/ha. This was the highest cadmium addition rate evaluated. [67]

A Japanese study published in 1990 found that yield of wheat plants did not exhibit phytotoxic effects when grown in soil containing cadmium at a concentration of 10 ppmw but did exhibit phytotoxic effects when grown in soil containing cadmium at concentrations of 30 ppmw or higher. [68]

A Dutch study published in 1989 found that lettuce plants exhibit no phytotoxic effects when grown in loam with a cadmium concentration as high as 3.2 ppmw; significant phytotoxic effects (representing 50 percent yield reduction) were observed at a cadmium concentration of 33 ppmw. The same study found that lettuce is significantly more sensitive to cadmium than are tomato plants (*Lycopersicum esculentum*) or oat plants (*Avena sativa*) when grown in loam, and that lettuce grown in loam is much more sensitive to cadmium than is lettuce grown in humic sand (pH 5.1). [69]

A Canadian study published in 1976 evaluated the cadmium uptake rate and the phytotoxic effect of cadmium on twelve different varieties of lettuce plants grown in sand and nutrient solution. The results of this study showed that effects varied considerably between varieties. The varieties with the

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[63] B. Huang et al. "Cadmium Uptake by Lettuce from Soil Amended with Phosphorus and Trace Element Fertilizers." *Water, Air, & Soil Pollution*. Volume 147. July 2003. pp. 109-127.
[64] B. Huang et al. "Availability of Cadmium in Some Phosphorus Fertilizers to Field-Grown Lettuce." *Water, Air, & Soil Pollution*. Volume 158. October 2004. pp. 37-51.
[65] E. Lehoczky et al. "Heavy Metal Uptake by Ryegrass, Lettuce and White Mustard Plants on Different Soils." Presented at the *17th World Congress of Soil Science*. Bangkok, Thailand. August 2002.
[66] Kim Won-Il et al. "Effect of Cadmium and Arsenic in Soils on Growth and Availability to Vegetables." Presented at the *17th World Congress of Soil Science*. Bangkok, Thailand. August 2002.
[67] *A Report on the Plant Uptake of Metals from Fertilizers.* Washington State Department of Agriculture. December 2001.
[68] S. Muramoto et al. "The Critical Levels and the Maximum Metal Uptake for Wheat and Rice Plants when Appling Metal Oxides to Soil." *Journal of Environmental Science and Health, Part B.* Volume 25. 1990. pp. 273-280.
[69] D.M.M. Adema and L. Henzen. "A Comparison of Plant Toxicities of Some Industrial Chemicals in Soil Culture and Soilless Culture." *Ecotoxicology and Environmental Safety.* Volume 18. 1989. pp. 219-229.

lowest rates of absorption (leaf lettuce cv. "Early Prize Head" and head lettuce cv. "New York 12") had a plant tissue cadmium concentration less than half that of the variety with the highest rate of uptake (head lettuce cv. "Great Lakes 428"). Similarly, when grown with a nutrient solution containing 0.5 ppmw cadmium, the least sensitive variety (head lettuce cv. "New York 12") exhibited a 28 percent increase in yield, whereas the most sensitive variety (head lettuce cv. "Great Lakes 428") experienced a 32 percent decrease in yield. [70]

An American study published in 1978 found that lettuce plants exhibited no phytotoxic effects when grown in acid soil (fine sandy loam, pH 5.7) with a cadmium concentration as high as 20 ppmw, but did exhibit phytotoxic effects when grown in the same soil with a cadmium concentration of 40 ppmw or higher. In calcareous soil (silt loam, pH 7.5), the lettuce plants exhibited no phytotoxic effects up to a cadmium concentration of 10 ppmw, but did exhibit phytotoxic effects at a cadmium concentration of 20 ppmw or higher. [71]

The same study found that wheat plants exhibited no phytotoxic effects with a soil cadmium concentration as high as 20 ppmw, but did exhibit phytotoxic effects at a cadmium concentration of 40 ppmw or higher. This result was consistent using both acidic and calcareous soils. [72]

An American study published in 1975 found that the following soil cadmium concentrations produced significant phytotoxic effects (represented by 25 percent decrease in yield) in agricultural crops: in spinach plants, 4 ppmw; in lettuce plants, 13 ppmw; and in wheat plants, 50 ppmw. Spinach was the most sensitive of fourteen crops studied. [73]

An American study published in 1973 found that yield of wheat plants was slightly reduced, and yield of lettuce plants was significantly reduced, by soil cadmium concentrations as low as 2.5 ppmw. [74]

A Canadian study published in 1973 found that yield of spinach plants was significantly reduced when grown in soil with a cadmium concentration of 40 ppmw. The same study found that yields of lettuce plants and broccoli plants were not reduced when grown in soil with a cadmium concentration of 40 ppmw, but were significantly reduced at a soil cadmium concentration of 200 ppmw. [75]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's cadmium emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or on human health effects due to uptake by crops. The maximum predicted

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[70] M.K. John and C.J. van Laerhoven. "Differential Effects of Cadmium on Lettuce Varieties." *Environmental Pollution.* Volume 10. 1976. pp. 163-173.
[71] G.A. Mitchell et al. "Yield and Metal Composition of Lettuce and Wheat Grown on Soils Amended with Sewage Sludge Enriched with Cadmium, Copper, Nickel, and Zinc." *Journal of Environmental Quality.* Volume 7. 1978. pp. 165-171.
[72] Ibid.
[73] F.T. Bingham et al. "Growth and Cadmium Accumulation of Plants Grown on a Soil Treated with a Cadmium-Enriched Sewage Sludge." *Journal of Environmental Quality.* Volume 4. 1975. pp. 207-211.
[74] F. Haghiri. "Cadmium Uptake by Plants." *Journal of Environmental Quality.* Volume 2. 1973. pp. 93-95.
[75] M.K. John. "Cadmium Uptake by Eight Food Crops as Influenced by Various Soil Levels of Cadmium." *Environmental Pollution.* Volume 4. 1973. pp. 7-15.

cadmium deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

H. Chromium

The maximum predicted deposition rate of total chromium is 0.00032 kg/ha·yr, the maximum 100-year deposition is 0.032 kg/ha, and the maximum 100-year increase in soil concentration is 0.000017 ppmw. The concentration value is more than five orders of magnitude below the minimum U.S. EPA screening value of 8.4 ppmw.[76] There are no NAAQS for chromium.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of chromium will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to chromium uptake by agricultural crops. A summary of our findings follows.

Naturally occurring chromium concentrations in soils are generally in the range 1 ppmw to 1,400 ppmw, with a typical concentration of 55 ppmw.[77, 78]

In 2002, the World Health Organization adopted a maximum permissible soil concentration values for several pollutants, but did not establish one for chromium.[79] However, in its review, the organization identified guideline values established by eight different governments, including the European Union. The most stringent of these is a total deposition threshold of 60 kg/ha, established by four different governments.[80] This limit is nearly 2,000 times the maximum deposition expected from the refinery over a 100-year period.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 1 ppmw for chromium.[81] This value is based on phytotoxicity of several plants, including lettuce,[82] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

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[76] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.
[77] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.
[78] P.F. Pratt. "Chromium." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 136.
[79] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.
[80] Ibid. p. 31.
[81] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[82] Ibid. pp. 3-12 through 3-13.

In 1997, the National Park Service (within the U.S. Department of the Interior) reported that the maximum acceptable concentration of hexavalent chromium in soils used for production of food is 0.05 ppmw. [83]

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for chromium of 3,000 kg/ha. This limit is based on the level that was found to be adequate for avoiding phytotoxic effects, which is the most restrictive of all exposure pathways evaluated. For the "human home gardener" exposure pathway, assuming a lifetime of eating vegetables grown in chromium-contaminated soil, U.S. EPA did not identify a maximum cumulative loading limit; however, for the "child eating sewage sludge" exposure pathway, U.S. EPA determined that the maximum cumulative loading limit would be 79,000 kg/ha. [84]

A Dutch study published in 1989 found that lettuce plants may exhibit phytotoxic effects when grown in loam with a chromium concentration as low as 0.35 ppmw; significant phytotoxic effects (representing 50 percent yield reduction) were observed at a chromium concentration of 1.8 ppmw. The same study found that lettuce is significantly more sensitive to chromium than are tomato plants (*Lycopersicum esculentum*) or oat plants (*Avena sativa*) when grown in loam, and that lettuce grown in loam is much more sensitive to chromium than is lettuce grown in humic sand (pH 5.1). [85]

A California study published in 1978 found that *Gossypium barbadense* cotton plants did not exhibit any phytotoxic effects when grown in soil with chromium concentrations up to and including 50 ppmw; slight phytotoxic effects were observed at a chromium concentration of 100 ppmw. [86]

According to a 1966 textbook, studies of various agricultural crops have found that sensitive crops, such as tobacco, corn, oats, and barley, exhibit symptoms of phytotoxicity when grown in soil with a chromium concentration as low as 5 ppmw. [87]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's chromium emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to chromium uptake by agricultural crops. The maximum predicted chromium deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

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[83] R.J. Irwin et al. *Environmental Contaminants Encyclopedia – Chromium (in General) Entry.* U.S. Department of Energy, National Park Service, Water Resources Division, Water Operations Branch. Fort Collins, CO. July 1997. pp. 50-51.

[84] *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.

[85] D.M.M. Adema and L. Henzen. "A Comparison of Plant Toxicities of Some Industrial Chemicals in Soil Culture and Soilless Culture." *Ecotoxicology and Environmental Safety.* Volume 18. 1989. pp. 219-229.

[86] F.I. Rehab and A. Wallace. "Excess Trace Metal Effects on Cotton: 4. Chromium and Lithium in Yolo Loam Soil." *Communications in Soil Science and Plant Analysis.* Volume 9. 1978. pp. 645-651.

[87] P.F. Pratt. "Chromium." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. pp. 136-137.

I. Copper

The maximum predicted deposition rate of copper is 0.00015 kg/ha·yr, the maximum 100-year deposition is 0.015 kg/ha, and the maximum 100-year increase in soil concentration is 0.0000083 ppmw. The concentration value is more than six orders of magnitude below the minimum U.S. EPA screening value of 40 ppmw.[88] There are no NAAQS for copper.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of copper will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to copper uptake by agricultural crops. A summary of our findings follows.

Copper is an essential nutrient for most plants.[89] Naturally occurring copper concentrations in soils are generally in the range 1 ppmw to 300 ppmw, with a typical concentration of 22 ppmw.[90, 91]

In 2002, the World Health Organization adopted a maximum permissible soil concentration values for several pollutants, but did not establish one for copper.[92] However, in its review, the organization identified guideline values established by thirteen different governments, including the European Union. The most stringent of these is a total deposition threshold of 40 kg/ha, established by the governments of Denmark and Sweden.[93] This limit is nearly 3,000 times the maximum deposition expected from the refinery over a 100-year period.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 100 ppmw for copper.[94] This value is primarily based on phytotoxicity of little bluestem[95] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

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[88] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.

[89] W. Reuther and C.K. Labanauskas. "Copper." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 165.

[90] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.

[91] W. Reuther and C.K. Labanauskas. "Copper." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 165.

[92] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.

[93] Ibid. p. 31.

[94] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.

[95] Ibid. p. 3-15.

In 1997, the National Park Service (within the U.S. Department of the Interior) reported the following with respect to copper contamination of soils:

- The maximum acceptable concentration of copper in soils used for production of food is 23 ppmw. [96]
- Seven states were identified as having standards limiting the cumulative application of copper to soils. The most stringent of the identified standards is 84 kg/ha, for agricultural soils in New York State. [97]
- Spinach plants exhibit phytotoxic effects when grown in soil containing copper at a concentration of 98 ppmw. [98]
- Citrus trees exhibit phytotoxic effects when grown in soil containing copper at concentrations as low as 15 ppmw. [99]
- No adverse human health effects are expected for humans, including children, residing adjacent to soil containing copper at a concentration of 74 ppmw. [100]

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for copper of 1,500 kg/ha. This limit is based on the level that was found to be adequate for avoiding phytotoxic effects, which is the most restrictive of all exposure pathways evaluated. For the "human home gardener" exposure pathway, assuming a lifetime of eating vegetables grown in copper-contaminated soil, U.S. EPA did not identify a maximum cumulative loading limit; however, for the "child eating sewage sludge" exposure pathway, U.S. EPA determined that the maximum cumulative loading limit for copper would be 10,000 kg/ha. [101]

A Swedish study published in 2004 found that germination of lettuce plants in sewage sludge was not affected by the presence of copper at a concentration of 500 ppmw. [102]

A California study published in 1978 found that *Gossypium barbadense* cotton plants did not exhibit any phytotoxic effects when grown in soil with copper concentrations up to and including 100 ppmw; significant phytotoxic effects were observed at a copper concentration of 400 ppmw. [103]

A Canadian study published in 1978 found that lettuce plants exhibited no phytotoxic effects when grown in clay soil (pH 5.9) with a copper concentration as high as 480 ppmw, which was the highest copper concentration evaluated. In loam soil (pH 6.3), the lettuce plants exhibited slightly decreased

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[96] R.J. Irwin et al. *Environmental Contaminants Encyclopedia – Copper Entry.* U.S. Department of Energy, National Park Service, Water Resources Division, Water Operations Branch. Fort Collins, CO. July 1997. p. 48.
[97] Ibid. pp. 45-46.
[98] Ibid. p. 49.
[99] Ibid. p. 49.
[100] Ibid. p. 49.
[101] *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.
[102] B. Fjällborg and G. Dave. "Toxicity of Sb and Cu in Sewage Sludge to Terrestrial Plants (Lettuce, Oat, Radish) and of Sludge Elutriate to Aquatic Organisms (*Daphnia* and *Lemna*) and its Interactions." *Water, Air, & Soil Pollution*. Volume 155. June 2004. pp. 3-20.
[103] F.I. Rehab and A. Wallace. "Excess Trace Metal Effects on Cotton: 2. Copper, Zinc, Cobalt and Manganese in Yolo Loam Soil." *Communications in Soil Science and Plant Analysis.* Volume 9. 1978. pp. 519-527.

yield at a copper concentration of 30 ppmw, which was the lowest copper addition rate evaluated, and significantly decreased yield at a copper concentration of 60 ppmw. [104]

An American study published in 1978 found that lettuce plants exhibited no phytotoxic effects when grown in acid soil (fine sandy loam, pH 5.7) with a copper concentration as high as 160 ppmw, but did exhibit phytotoxic effects when grown in the same soil with a copper concentration of 320 ppmw or higher. In calcareous soil (silt loam, pH 7.5), the lettuce plants exhibited no phytotoxic effects up to a copper concentration of 80 ppmw, but did exhibit phytotoxic effects at a copper concentration of 160 ppmw or higher. [105]

The same study found that wheat plants exhibited no phytotoxic effects when grown in acid soil (fine sandy loam, pH 5.7) with a copper concentration as high as 80 ppmw, but did exhibit phytotoxic effects at a copper concentration of 160 ppmw or higher. In calcareous soil (silt loam, pH 7.5), the wheat plants exhibited no phytotoxic effects up to a copper concentration of 160 ppmw, but did exhibit phytotoxic effects at a copper concentration of 320 ppmw or higher. [106]

A study published in 1953 found that citrus seedlings exhibit symptoms of phytotoxicity when grown in soil with a copper concentration of 150 ppmw. [107]

A study published in 1953 found that spinach plants exhibit symptoms of phytotoxicity when grown in soil with a copper concentration of 98 ppmw and above. [108]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's copper emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to copper uptake by agricultural crops. The maximum predicted copper deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

J. Lead

Based on the results of the air quality impacts analysis, as described in Table VII-7 of the Technical Support Document, the maximum predicted impacts on ambient lead concentration due to emissions from the refinery are 0.0288 $\mu g/m^3$ on a daily average and 0.00042 $\mu g/m^3$ on an annual average. These are well below the secondary NAAQS of 1.5 $\mu g/m^3$ on a calendar-quarter average.

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[104] A.J. MacLean and A.J. Dekker. "Availability of Zinc, Copper, and Nickel to Plants Grown in Sewage-Treated Soils." *Canadian Journal of Soil Science.* Volume 58. 1978. pp. 381-389.
[105] G.A. Mitchell et al. "Yield and Metal Composition of Lettuce and Wheat Grown on Soils Amended with Sewage Sludge Enriched with Cadmium, Copper, Nickel, and Zinc." *Journal of Environmental Quality.* Volume 7. 1978. pp. 165-171.
[106] Ibid.
[107] W. Reuther and C.K. Labanauskas. "Copper." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 171.
[108] W. Reuther and C.K. Labanauskas. "Copper." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 174.

The maximum predicted deposition rate of lead is 0.00035 kg/ha·yr, the maximum 100-year deposition is 0.035 kg/ha, and the maximum 100-year increase in soil concentration is 0.000019 ppmw. The concentration value is more than four orders of magnitude below the minimum U.S. EPA screening value of 1,000 ppmw. [109]

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of lead will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to lead uptake by agricultural crops. A summary of our findings follows.

Naturally occurring lead concentrations in soils are generally in the range 1.5 ppmw to 280 ppmw, with a typical concentration of 25 ppmw. [110, 111] However, most of this lead is insoluble and not available to plants; the typical concentration of "soluble" or "available" lead is in the range 0.05 ppmw to 5 ppmw. [112]

In 2002, the World Health Organization adopted a maximum soil concentration screening value of 83.9 ppmw for lead. [113] In establishing this value, the organization identified guideline values established by thirteen different governments, including the U.S. and the European Union. The most stringent limit is a total deposition threshold of 40 kg/ha, established by the governments of Denmark and Sweden. [114] This limit is more than 1,000 times the maximum deposition expected from the refinery over a 100-year period.

In Canada, the maximum acceptable level for cumulative lead additions to soil is 100 kg/ha. [115] This standard, which was initially adopted in 1979 and was most recently reaffirmed in 1997, is intended to protect against risk to humans, plants, and animals. [116] The Canadian standard is nearly 3,000 times the maximum deposition expected from the refinery over a 100-year period.

[109] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.
[110] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.
[111] R.F. Brewer. "Lead." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 216.
[112] Ibid.
[113] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.
[114] Ibid. p. 31.
[115] *Guidelines to the Fertilizers Act and Regulations, 2nd Ed.* Agriculture and Agri-Food Canada. Nepean, Ontario, Canada. November 1996. p. 3-3.
[116] Ibid.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 50 ppmw for lead. [117] This value is primarily based on phytotoxicity in oak and sycamore trees [118] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

In 1997, the National Park Service (within the U.S. Department of the Interior) reported the following with respect to lead contamination of soils:

- The maximum acceptable concentration of lead in soils used for production of food is 20 ppmw. [119]
- Seven states were identified as having standards limiting the cumulative application of lead to soils. The most stringent of the identified standards is 336 kg/ha, for agricultural soils in New York State. [120]
- No adverse human health effects are expected for humans, including children, residing adjacent to soil containing lead at a concentration of 400 ppmw. [121]

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for lead of 300 kg/ha. This limit is based on the level that was found to be safe for a child ingesting biosolids, which is the most restrictive of all exposure pathways evaluated. U.S. EPA did not identify maximum cumulative loading limits for the "child ingesting sewage sludge" exposure pathway or the "human home gardener" exposure pathway. [122]

A Hungarian study presented in 2002 found that lettuce plants did not exhibit any phytotoxic effects when grown in soil with a total lead concentration of 188 ppmw and an available lead concentration of 72 ppmw, but did exhibit phytotoxicity when grown in soil with a total lead concentration of 1,232 ppmw and an available lead concentration of 386 ppmw. [123]

A study commissioned by the Washington State Department of Agriculture and published in 2001 found that yield of lettuce plants was not affected by addition of lead to soil at rates as high as 89 kg/ha. This was the highest lead addition rate evaluated. [124]

[117] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[118] Ibid. pp. 3-17 through 3-18.
[119] R.J. Irwin et al. *Environmental Contaminants Encyclopedia – Lead Entry.* U.S. Department of Energy, National Park Service, Water Resources Division, Water Operations Branch. Fort Collins, CO. July 1997. p. 47.
[120] Ibid. pp. 43-45.
[121] Ibid. p. 47.
[122] *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.
[123] E. Lehoczky et al. "Heavy Metal Uptake by Ryegrass, Lettuce and White Mustard Plants on Different Soils." Presented at the *17th World Congress of Soil Science*. Bangkok, Thailand. August 2002.
[124] *A Report on the Plant Uptake of Metals from Fertilizers.* Washington State Department of Agriculture. December 2001.

A Japanese study published in 1990 found that yield of wheat plants did not exhibit phytotoxic effects when grown in soil containing lead at concentrations up to and including 3,000 ppmw but did exhibit phytotoxic effects when grown in soil containing lead at concentrations of 10,000 ppmw or higher. [125]

A Canadian study published in 1972 found that lettuce plants exhibited phytotoxic effects when grown in soil containing lead at a concentration of 1,000 ppmw. Similar results were obtained when using lead chloride ($PbCl_2$), lead carbonate ($PbCO_3$), and lead nitrate ($Pb(NO_3)_2$). [126]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's lead emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to lead uptake by agricultural crops. The maximum predicted lead deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

K. Manganese

The maximum predicted deposition rate of manganese is 0.031 kg/ha·yr, the maximum 100-year deposition is 3.1 kg/ha, and the maximum 100-year increase in soil concentration is 0.0017 ppmw. This concentration value is more than three orders of magnitude below the minimum U.S. EPA screening value of 2.5 ppmw. [127] There are no NAAQS for manganese.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of manganese will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to manganese uptake by agricultural crops. A summary of our findings follows.

Manganese is an essential nutrient for most plants. [128] Naturally occurring manganese concentrations in soils are generally in the range 20 ppmw to 10,000 ppmw, with a typical concentration of 1,000 ppmw. [129, 130]

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 500 ppmw for manganese. [131] This value is primarily based on phytotoxicity of bush beans [132] and represents the

[125] S. Muramoto et al. "The Critical Levels and the Maximum Metal Uptake for Wheat and Rice Plants when Appling Metal Oxides to Soil." *Journal of Environmental Science and Health, Part B.* Volume 25. 1990. pp. 273-280.

[126] M.K. John and C.J. van Laerhoven. "Lead Uptake by Lettuce and Oats as Affected by Lime, Nitrogen, and Sources of Lead." *Journal of Environmental Quality.* Volume 1. 1972. pp. 169-171.

[127] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.

[128] C.K. Labanauskas. "Manganese." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 272.

[129] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.

[130] C.K. Labanauskas. "Manganese." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 272.

concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

A German study published in 1999 found that cowpea plants are highly tolerant of manganese, with only slight phytotoxic effects when grown in nutrient solution containing 50×10^{-6} molar (50 µM) manganese. [133]

A California study published in 1978 found that *Gossypium barbadense* cotton plants exhibited slight phytotoxic effects when grown in soil with a manganese concentrations of 500 ppmw, which was the lowest concentration evaluated; significant phytotoxic effects were observed at manganese concentrations of 1,000 ppmw and higher. [134]

A German study published in 1977 found that lettuce plants treated with a dust containing cadmium, copper, lead, and manganese did not absorb manganese, but did absorb the other three metals. [135]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's manganese emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to manganese uptake by agricultural crops. The maximum predicted manganese deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

L. Mercury

The maximum predicted deposition rate of mercury is 0.0065 kg/ha·yr, the maximum 100-year deposition is 0.65 kg/ha, and the maximum 100-year increase in soil concentration is 0.00036 ppmw. This concentration value is more than six orders of magnitude below the minimum U.S. EPA screening value of 455 ppmw. [136] There are no NAAQS for mercury.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of mercury will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to mercury uptake by agricultural crops. A summary of our findings follows.

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[131] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[132] Ibid. pp. 3-12 through 3-13.
[133] W.J. Horst et al. "Physiology of Manganese Toxicity and Tolerance in *Vigna Unguiculata* (L.) Walp." *Journal of Plant Nutrition and Soil Science.* Volume 162. 1999. pp. 263-274.
[134] F.I. Rehab and A. Wallace. "Excess Trace Metal Effects on Cotton: 2. Copper, Zinc, Cobalt and Manganese in Yolo Loam Soil." *Communications in Soil Science and Plant Analysis.* Volume 9. 1978. pp. 519-527.
[135] G.H.M. Krause and H. Kaiser. "Plant Response to Heavy Metals and Sulphur Dioxide." *Environmental Pollution.* Volume 12. 1977. pp. 63-71.
[136] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.

Naturally occurring mercury concentrations in soils are generally in the range 0.004 ppmw to 1.5 ppmw, with a typical concentration of 0.08 ppmw. [137]

In 2002, the World Health Organization adopted a maximum soil concentration screening value of 7.41 ppmw for mercury. [138] In establishing this value, the organization identified guideline values established by ten different governments, including the European Union. The most stringent limit purportedly identified by the authors of the World Health Organization report is a total deposition threshold of 0.6 kg/ha, purportedly established by the government of Canada. [139] However, as discussed below, this does not reflect the limit actually in effect in Canada. The second most stringent limit identified by the authors of the World Health Organization report is a total deposition threshold of 0.8 kg/ha, established by the governments of Denmark and Sweden. [140] This limit is approximately 20 percent higher than the maximum deposition expected from the refinery over a 100-year period.

In Canada, the maximum acceptable level for cumulative mercury additions to soil is 1 kg/ha. [141, 142] This standard, which were initially adopted in 1979 and were most recently reaffirmed in 1997, are intended to protect against risk to humans, plants, and animals. [143] The Canadian standard is approximately 50 percent higher than the maximum deposition expected from the refinery over a 100-year period.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 0.3 ppmw for mercury. [144] This value represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

In 1997, the National Park Service (within the U.S. Department of the Interior) reported the following with respect to mercury contamination of soils:

- The maximum acceptable concentration of mercury in soils used for production of food is 2.1 ppmw. [145]

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[137] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.
[138] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.
[139] Ibid. p. 31.
[140] Ibid. p. 31.
[141] *Guidelines to the Fertilizers Act and Regulations, 2nd Ed.* Agriculture and Agri-Food Canada. Nepean, Ontario, Canada. November 1996. p. 3-3.
[142] *Trade Memorandum T-4-93e: Standards for Metals in Fertilizers and Supplements.* Canadian Food Inspection Agency, Plant Products Directorate, Plant Production Division, Fertilizer Section. Nepean, Ontario, Canada. September 1997.
[143] Ibid.
[144] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.

- Vermont's standard limiting the cumulative application of mercury to soils is 6 kg/ha. [146]

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for mercury of 17 kg/ha. This limit is based on the level that was found to be safe for a child ingesting biosolids, which is the most restrictive of all exposure pathways evaluated. For the "human home gardener" exposure pathway, assuming a lifetime of eating vegetables grown in mercury-contaminated soil, U.S. EPA determined that the maximum cumulative loading limit would be 370 kg/ha. A loading limit based on phytotoxicity was not determined. [147]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's mercury emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to mercury uptake by agricultural crops. The maximum predicted mercury deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

M. Nickel

The maximum predicted deposition rate of nickel is 0.000033 kg/ha·yr, the maximum 100-year deposition is 0.0033 kg/ha, and the maximum 100-year increase in soil concentration is 0.0000018 ppmw. The concentration value is more than eight orders of magnitude below the minimum U.S. EPA screening value of 500 ppmw. [148] There are no NAAQS for nickel.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of nickel will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to nickel uptake by agricultural crops. A summary of our findings follows.

Naturally occurring nickel concentrations in soils are generally in the range 0.2 ppmw to 500 ppmw, with a typical concentration of 21 ppmw. [149, 150]

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145 R.J. Irwin et al. *Environmental Contaminants Encyclopedia – Mercury Entry.* U.S. Department of Energy, National Park Service, Water Resources Division, Water Operations Branch. Fort Collins, CO. July 1997. p. 47.

146 Ibid. p. 43.

147 *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.

148 A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.

149 A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.

150 A.P. Vanselow. "Nickel." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 303.

In 2002, the World Health Organization adopted a maximum soil concentration screening value of 107.26 ppmw for nickel. [151] In establishing this value, the organization identified guideline values established by eleven different governments, including the U.S. and the European Union. The most stringent limit is a total deposition threshold of 20 kg/ha, established by the governments of Spain and Norway. [152] This limit is more than 6,000 times the maximum deposition expected from the refinery over a 100-year period.

In Canada, the maximum acceptable level for cumulative nickel additions to soil is 36 kg/ha. [153] This standard, which was initially adopted in 1979 and was most recently reaffirmed in 1997, is intended to protect against risk to humans, plants, and animals. [154] The Canadian standard is more than four orders of magnitude times the maximum deposition expected from the refinery over a 100-year period.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 30 ppmw for nickel. [155] This value is primarily based on phytotoxicity of barley [156] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for nickel of 420 kg/ha. This limit is based on the level that was found to be adequate for avoiding phytotoxic effects, which is the most restrictive of all exposure pathways evaluated. For the “human home gardener” exposure pathway, assuming a lifetime of eating vegetables grown in nickel-contaminated soil, U.S. EPA determined that the maximum cumulative loading limit would be 10,000 kg/ha. [157]

A Canadian study published in 1978 found that lettuce plants exhibited no phytotoxic effects when grown in clay soil (pH 5.9) with a nickel concentration as high as 480 ppmw, which was the highest nickel concentration evaluated. In loam soil (pH 6.3), the yield of lettuce plants decreased at a nickel concentration of 30 ppmw, which was the lowest nickel addition rate evaluated. [158]

An American study published in 1978 found that lettuce plants exhibited no phytotoxic effects when grown in acid soil (fine sandy loam, pH 5.7) with a nickel concentration as high as 640 ppmw, which was the highest concentration tested. In calcareous soil (silt loam, pH 7.5), the lettuce plants exhibited

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[151] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.
[152] Ibid. p. 31.
[153] *Guidelines to the Fertilizers Act and Regulations, 2nd Ed.* Agriculture and Agri-Food Canada. Nepean, Ontario, Canada. November 1996. p. 3-3.
[154] Ibid.
[155] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[156] Ibid. pp. 3-24 through 3-25.
[157] *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.
[158] A.J. MacLean and A.J. Dekker. “Availability of Zinc, Copper, and Nickel to Plants Grown in Sewage-Treated Soils.” *Canadian Journal of Soil Science.* Volume 58. 1978. pp. 381-389.

no phytotoxic effects up to a nickel concentration of 160 ppmw, but did exhibit phytotoxic effects at a nickel concentration of 320 ppmw or higher. [159]

The same study found that wheat plants exhibited no phytotoxic effects when grown in acid soil (fine sandy loam, pH 5.7) with a nickel concentration as high as 40 ppmw, but did exhibit phytotoxic effects at a nickel concentration of 80 ppmw or higher. In calcareous soil (silt loam, pH 7.5), the wheat plants exhibited no phytotoxic effects up to a nickel concentration of 160 ppmw, but did exhibit phytotoxic effects at a nickel concentration of 320 ppmw or higher. [160]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's nickel emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to nickel uptake by agricultural crops. The maximum predicted nickel deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

N. Selenium

The maximum predicted deposition rate of selenium is 0.019 kg/ha·yr, the maximum 100-year deposition is 1.9 kg/ha, and the maximum 100-year increase in soil concentration is 0.0011 ppmw. The concentration value is more than five orders of magnitude below the minimum U.S. EPA screening value of 500 ppmw. [161] There are no NAAQS for selenium.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of selenium will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to selenium uptake by agricultural crops. A summary of our findings follows.

Naturally occurring selenium concentrations in soils are generally in the range 0.05 ppmw to 6 ppmw, with a typical concentration of 0.3 ppmw. [162, 163]

In 2002, the World Health Organization adopted a maximum soil concentration screening value of 6.16 ppmw for selenium. [164]

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[159] G.A. Mitchell et al. "Yield and Metal Composition of Lettuce and Wheat Grown on Soils Amended with Sewage Sludge Enriched with Cadmium, Copper, Nickel, and Zinc." *Journal of Environmental Quality.* Volume 7. 1978. pp. 165-171.
[160] Ibid.
[161] A.E. Smith and J.B. Levenson. *A Screening Procedure for the Impacts of Air Pollution Sources on Plants, Soils, and Animals (EPA-450/2-81-078).* U.S. EPA, Office of Air Quality Planning and Standards. Research Triangle Park, NC. December 1980. p. 17.
[162] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.
[163] T.J. Ganje. "Selenium." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 400.
[164] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.

In Canada, the maximum acceptable level for cumulative selenium additions to soil is 2.8 kg/ha. [165] This standard, which was initially adopted in 1979 and was most recently reaffirmed in 1997, is intended to protect against risk to humans, plants, and animals. [166] The Canadian standard is approximately 50 percent higher than the maximum deposition expected from the refinery over a 100-year period.

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 1 ppmw for selenium. [167] This value is primarily based on phytotoxicity of sorghum plants [168] and represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

In 1993, in the context of its regulations governing land application of sewage sludge, the U.S. EPA established a maximum cumulative loading limit for selenium of 100 kg/ha. This limit is based on the level that was found to be safe for a child ingesting biosolids, which is the most restrictive of all exposure pathways evaluated. For the "human home gardener" exposure pathway, assuming a lifetime of eating vegetables grown in selenium-contaminated soil, and for the "human eating animals fed crops grown on selenium-contaminated soils" exposure pathway, assuming a lifetime of eating potentially selenium-contaminated meat, U.S. EPA determined that the maximum cumulative loading limits would be 1,200 kg/ha and 15,000 kg/ha, respectively. A loading limit based on phytotoxicity was not determined. [169]

In 1997, the National Park Service (within the U.S. Department of the Interior) reported that no adverse human health effects are expected for humans, including children, residing adjacent to soil containing selenium at a concentration of 10 ppmw. [170]

A study performed in India and published in 1978 found that yield of wheat plants was adversely affected when grown in soil with a selenium concentration as low as 2.5 ppmw. [171]

A study published in 1934 found that wheat plants exhibit symptoms of phytotoxicity when grown in soil with a selenium concentration of 30 ppmw and above. [172]

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[165] *Guidelines to the Fertilizers Act and Regulations, 2nd Ed.* Agriculture and Agri-Food Canada. Nepean, Ontario, Canada. November 1996. p. 3-3.
[166] Ibid.
[167] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.
[168] Ibid. p. 3-26.
[169] *A Guide to the Biosolids Risk Assessments for the EPA Part 503 Rule* (EPA-832/B-93-005). U.S. EPA, Office of Water Management. Washington, DC. September 1995. pp. 82-99.
[170] R.J. Irwin et al. *Environmental Contaminants Encyclopedia – Selenium Entry.* U.S. Department of Energy, National Park Service, Water Resources Division, Water Operations Branch. Fort Collins, CO. July 1997. pp. 51-52.
[171] M. Singh and N. Singh. "Selenium Toxicity in Plants and its Detoxification by Phosphorus." *Soil Science.* Volume 126. 1978. pp. 255-262.
[172] T.J. Ganje. "Selenium." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. p. 401.

A study published in 1937 found that cotton plants did not exhibit any symptoms of phytotoxicity when grown in soil with a selenium concentration of 10 ppmw or less, but did exhibit symptoms of phytotoxicity when grown in soil with a selenium concentration of 20 ppmw and above. [173]

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's selenium emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to selenium uptake by agricultural crops. The maximum predicted selenium deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

O. Silver

The maximum predicted deposition rate of silver is 0.0015 kg/ha·yr, the maximum 100-year deposition is 0.15 kg/ha, and the maximum 100-year increase in soil concentration is 0.00085 ppmw. There are no NAAQS or U.S. EPA screening values for silver.

We reviewed the literature to ascertain whether there exists, in the scientific literature, any basis for concluding that the refinery's emissions of silver will have an unacceptable phytotoxic impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to silver uptake by agricultural crops. A summary of our findings follows.

Naturally occurring silver concentrations in soils are generally in the range 0.01 ppmw to 8 ppmw, with a typical concentration of 0.05 ppmw. [174, 175]

In 2002, the World Health Organization adopted a maximum soil concentration screening value of 3.37 ppmw for silver. [176]

In 1997, the National Park Service (within the U.S. Department of the Interior) reported the following with respect to silver contamination of soils:

- Most agricultural crops, including spinach plants, exhibit no phytotoxic effects when grown in soil containing silver at a concentration of 100 ppmw. [177]
- Lettuce plants grown in soil containing silver at a concentration of 10 ppmw exhibited phytotoxic effects. [178]

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[173] Ibid.

[174] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. p. 27.

[175] A.P. Vanselow. "Silver." In *Diagnostic Criteria for Plants and Soils. University of California, Division of Agricultural Sciences*. H.D. Chapman, ed. Riverside, CA. 1966. pp. 405-407.

[176] A.C. Chang, et al. *Developing Human Health-related Chemical Guidelines for Reclaimed Water and Sewage Sludge Applications in Agriculture.* World Health Organization. Copenhagen, Denmark. May 2002. pp. iv and 71.

[177] R.J. Irwin et al. *Environmental Contaminants Encyclopedia – Silver Entry.* U.S. Department of Energy, National Park Service, Water Resources Division, Water Operations Branch. Fort Collins, CO. July 1997. p. 38.

- No adverse human health effects are expected for humans, including children, residing adjacent to soil containing silver at a concentration of 10 ppmw. [179]

In 2002, the World Health Organization reported the results of a study that found that spinach plants and several other agricultural crops did not exhibit any phytotoxic effects when grown in soil containing soil with a silver concentration of 106 ppmw, which was the highest concentration tested. The same study found that lettuce did not exhibit phytotoxic effects at a soil concentration of 5 ppmw, but did exhibit phytotoxic effects at soil concentrations of 14 ppmw and higher. [180]

In 1997, the U.S. Department of Energy instituted a soil concentration screening value of 2 ppmw for silver. [181] This value represents the concentration that the authors consider adequate to ensure that no phytotoxic effects will occur in terrestrial plants grown in soil.

Nothing in the scientific literature identified during this supplemental review would indicate that the refinery's silver emissions will have an unacceptable, adverse impact on agricultural crops grown near the refinery site or an unacceptable risk of human health effects due to silver uptake by agricultural crops. The maximum predicted silver deposition rate will not lead to soil concentrations that are identified in the literature as being harmful to crops or to people that consume affected crops.

III. Summary and Conclusions

The refinery's emissions, and the effects of those emissions on soils and agricultural crops, are acceptable. For each pollutant of concern, the predicted ambient concentration or the predicted deposition rate are well below the secondary NAAQS and the minimum screening values established by U.S. EPA, as established previously. Nothing in the scientific literature identified during this supplemental review would indicate that the secondary NAAQS and the minimum U.S. EPA screening values are not protective of any identified crops and, where no secondary NAAQS or screening values have been established, the predicted ambient concentration or the predicted deposition rate is less than the screening values established by other governmental authorities.

The results of this supplemental review are summarized in the Tables 1 and 2.

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[178] Ibid.
[179] Ibid. p. 41.
[180] *Silver and Silver Compounds: Environmental Aspects.* World Health Organization. Geneva, Switzerland. 2002. p. 19.
[181] R.A. Efroymson et al. *Technological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision.* U.S. Department of Energy, Office of Environmental Management. Oak Ridge, TN. 1997. p. 2-5.

Table 1
Summary of Supplemental Review for Gaseous Pollutants
(all values µg/m^3)

	SO_2	NO_X	H_2S	NH_3	Tetrachloroethylene
ACF modeled concentration	115, 3-hr 52.3, daily 10.2, annual	5, annual	84.6, 1-hr 7.09, daily	2.49, 1-hr 0.497, daily	1.7, 1-hr 0.369, daily 0.282, annual
Concern levels:					
NAAQS	1300, 3-hr	100, annual	n/a	n/a	n/a
EPA Screening Value	786, 3-hr 18, annual	94, annual	28000, 4-hr	n/a	n/a
Foreign Guidelines	30, season	75, daily 30, annual	n/a	270, daily 8, annual	n/a
Scientific Literature	27, season	150, monthly	417, season	600, 16 days	172, daily 46, monthly

Table 2
Summary of Supplemental Review for Trace Metals
(all values ppmw unless otherwise specified)

	Al	Cd	Cr	Cu	Pb
ACF 100-year increase	0.045	0.0000047	0.000017	0.0000083	0.000019
Concern levels:					
EPA Screening Value	n/a	2.5	8.4	40	1,000
Foreign Guidelines	n/a	3.92	n/a	n/a	83.9
U.S. D.O.E. Value	50	4	1	100	50
Scientific Literature	0.7	4	0.35	15	20

	Mn	Hg	Ni	Se	Ag
ACF 100-year increase	0.0017	0.00036	0.0000018	0.0011	0.00085
Concern levels:					
EPA Screening Value	2.5	455	500	500	n/a
Foreign Guidelines	n/a	7.41	107.26	6.16	3.37
U.S. D.O.E. Value	500	0.3	30	1	2
Scientific Literature	500	2.1	30	2.5	n/a